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(71) Applicant: **ECC INTERNATIONAL LIMITED**
John Keay House
St. Austell Cornwall PL25 4DJ (GB)

(72) Inventor: **Goodman, Howard**
40 Turnavean Road
St. Austell Cornwall (GB)

(74) Representative: **Bull, Michael Alan et al**
Haseltine Lake & Co. Hazlitt House 28 Southampton Buildings Chancery Lane
London WC2A 1AT (GB)

(54) **Paper coating.**

(57) There is disclosed a paper, suitable for printing, comprising a cellulosic sheet material provided with first and second pigmented coats each of which is hydrophilic, water absorbent and porous, said first coat being a base coat and said second coat being a top coat; wherein the pigment of one of said coats is predominantly of non smectite-type nature, whilst the pigment of the other of the said coats is predominantly of a smectite-type nature comprising at least 60% by weight of a water-swellable smectite-type clay. Also disclosed is a method of preparing the paper and a method of printing on the paper.

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Descripti n

PAPER COATING

This invention relat s to coated paper suitable for printing by the rotogravure process or by offset lithography, and to methods of preparing the same.

THE PRIOR ART

GB-2039789 discloses an electrostatic imaging sheet wherein one side of the sheet is electrically conductive and the other side of the sheet has a continuous dielectric layer comprising a mixture of a smectite clay and an electrically insulating polymer.

THE INVENTION

According to a first aspect of the present invention there is provided a paper suitable for printing by offset lithography and/or by a rotogravure process, comprising a cellulosic sheet material provided with first and second pigmented coats each of which is hydrophilic, water absorbent and porous, said first coat being a base coat and said second coat being a top coat; wherein the pigment of one of said coats is predominantly of non smectite-type nature, whilst the pigment of the other of the said coats is predominantly of a smectite-type nature comprising at least 60% by weight of a water-swellable smectite-type clay.

According to a second aspect of the present invention there is provided a method of preparing paper suitable for printing by offset lithography and/or by a rotogravure process which method includes the steps of applying the following pigmented coats to a cellulosic sheet material;

(i) a first, or base, coat; and

(ii) a second, or top, coat; wherein the pigment of one of said coats is predominantly of non smectite-type nature and the pigment of the other of said coats is predominantly of a smectite-type nature comprising at least 60% by weight of a water-swellable smectite-type clay.

According to a third aspect of the present invention there is provided a method of printing an image on a paper, using a rotogravure or an offset lithography printing process, the paper on which the image is printed comprising a cellulosic sheet material provided with first and second pigmented coats each of which is hydrophilic, water absorbent and porous, said first coat being a base coat and said second coat being a top coat; wherein the pigment of one of said coats is predominantly of non smectite-type nature, whilst the pigment of the other of the said coats is predominantly of a smectite-type nature comprising at least 60% by weight of a water-swellable smectite-type clay.

In order to be suitable for use in an offset lithographic printing process, both the base coat and the top coat of a paper according to the present invention need to be hydrophilic, water absorbent and porous so that water can be transported rapidly away from the surface of the paper.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The smectite-type clay may, for example, be bentonite, montmorillonite, hectorite, saponite or fullers earth, but especially preferred is a natural bentonite which has, or has been treated to have, predominantly sodium ions in its exchangeable cation sites. Preferably, the pigment which is predominantly of a smectite-type nature contain at least 75%, more preferably at least 90%, by weight of the smectite-type clay.

The pigment employed in the other coating may, for example, be a white pigment, other than a smectite-type clay, such as a kaolin clay, a natural or a synthetic calcium carbonate, talc or a natural or synthetic calcium sulphate. Alternatively, other conventional pigments may be employed. It is possible that the pigment in the other coating may, in some instances, also contain a minor amount of a smectite-type clay.

The paper may be provided with further coatings. It is preferred however, that the material comprises two coatings, the top coating including a pigment which is predominantly smectite-type clay, typically bentonite, whilst the other coating, or base coating, includes a pigment which is substantially non-smectite in nature. It is, however, within the scope of the invention to provide a paper in which the pigment of the base coating is predominantly smectite clay in nature and the top coating substantially non-smectite clay. Most preferably, the base coating contains kaolin and the top coating bentonite.

Each of the coatings is preferably bound together by an adhesive which may, for instance, be one of the conventional adhesives used in paper coating, such as a rubber latex, for example an acrylic copolymer latex (styrene butadiene rubber latex), or a starch. When the pigment is not a smectite-type clay, the quantity of adhesive solids required is in the range of from 1 to 20 parts by weight to 100 parts by weight of the pigment. When the pigment is predominantly of a smectite type nature, the quantity of adhesive solids may be up to 300 parts by weight to 100 parts by weight of the pigment; in some circumstances, if the smectite-type coat is the base coat, the pigment may be employed in the absence of an adhesive as it has been found that adequate adhesion of the clay to the cellulosic fibres is achieved without the presence of an adhesive. When an adhesive is used it is found that for a paper intended for rotogravure printing a latex adhesive is preferred and especially an acrylic copolymer latex. Generally the quantity of adhesive used will be in the range from 1 to 300 parts by weight of dry polymer to 100 parts by weight of dry smectite clay.

Preferably, the pigment of the coat which is predominantly smectite-type in nature is provided by applying to the sheet material an aqueous suspension comprising up to 20% by weight of a pigment comprising at least

60% by weight of a water-swellable smectite clay.

DETAILED DESCRIPTION

The invention is further illustrated by the following Examples.

EXAMPLE 1

A rotogravure base paper of substance weight 38 gm^{-2} (grams per square metre) was coated by means of a laboratory coating apparatus of the type described in British Patent Specification No. 1032536 running at a speed of 200 m min^{-1}. Three different coating procedures were used, namely:-

1. A single coat of a composition consisting of 100 parts by weight of a kaolin clay, 5 parts by weight of an acrylic copolymer latex adhesive (dry basis), and water to form a suspension containing 57.4% by weight of total solids.

The kaolin clay had a particle size distribution such that 6% by weight consisted of particles having an equivalent spherical diameter larger than 10 microns and 43% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns. The latex contained 50% weight of acrylic copolymer solids.

Samples of the base paper were coated with the composition at four different coat weights.

2. a). A base coat of an aqueous suspension containing 5% by weight of the European bentonite having sodium and calcium exchangeable cations. The coat weight of bentonite applied to the base paper was 0.5 gm^{-2}.

b). A top coat of the same composition as was described under 1 above applied at four different coat weights.

3. a). A base coat of the same composition as was described under 1 above applied at four different coat weights.

b). A top coat of the same aqueous suspension of bentonite as was described under 2a. above at a coat weight of 0.5 gm^{-2}.

Samples of the hand-coated sheets were printed with test rotogravure prints on a Winstone proof press using the technique described in the article "Realistic paper tests for various printing processes" by A. Swan, published in "Printing Technology". Vol 13, No. 1, April 1969, pages 9-22. A gravure printing cylinder was used with an area of deeply etched cells to give a solid black area and an area of less deeply etched cells to give a half tone area. The gloss of the solid black areas on the tests prints was measured by the Tappi Standard Method No. T480 ts-65 and the print density of the solid black areas was determined according to the formula:-

Print density = $\log_{10}$ (1/reflectance)

Where the reflectance is the fraction of the incident light of wavelength 574 nm reflected back from the black area.

A further measurement of print density was performed on the reverse side of the paper in the region of the solid black area in order to determine the degree of "strike through" of the printing ink.

In addition, the degree of "speckle" in the half tone area of each print was determined by estimating the percentage of gravure printing dots which were missing from the test print. In addition the gloss of an un-printed area of each coated paper sample was also measured by the TAPPI Standard Method No. T480ts-65. The results obtained are set forth in Table I below:-

TABLE I

Coating procedure	Coat weight of kaolin composition (gm^{-2})	Gloss of unprinted paper	Gloss of solid black area	Print density		% missing dots (half tone area)
				solid black area	reverse of solid area	
1	2.2	34	51	1.74	0.26	4.6
1	3.6	42	55	1.76	0.26	3.4
1	5.7	49	48	1.64	0.25	2.4
1	7.2	52	50	1.67	0.22	1.2
2	1.6	32	64	1.95	0.24	4.7
2	2.7	34	65	1.94	0.24	5.1
2	5.7	41	60	1.82	0.24	2.5
2	8.1	46	54	1.70	0.24	1.9
3	2.7	36	65	1.98	0.22	5.1
3	4.1	43	73	2.06	0.21	3.3
3	6.2	48	75	2.11	0.20	2.4
3	7.7	50	73	2.08	0.19	1.0

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These results show that the application of a coating of 0.5 gm^{-2} of bentonite to the base paper as one coat in a two-coat procedure effects an increase in the gloss and print density of the solid black printed area. When the bentonite is applied as a base coat the increase is relatively small but when the bentonite suspension is applied as a top coat over a coating containing kaolin the increase in both gloss and print density is surprisingly large even though the gloss of the un-printed area is substantially unaffected by the presence of th bentonite. The half-tone print qualities, as indicated by the percentage of missing dots, are also substantially unaffected by the presence of the bentonite coating.

EXAMPLE 2

An offset base paper of substance weight 65 gm^{-2} was coated by means of the laboratory coating apparatus used in Example 1 running at a speed of 400 m min^{-1} firstly with a composition consisting of:
100 parts by weight of a kaolin clay
11 parts by weight of styrene butadiene rubber latex (dry basis)
1 part by weight of sodium carboxymethyl cellulose;
water to form a suspension containing 60.8% by weight of total solids

The kaolin clay had a particle size distribution such that 0.2% by weight consisted of particles having an equivalent spherical diameter larger than 10 microns and 10% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns. The latex contained 50% by weight of styrene butadiene rubber solids. Samples of the base paper were coated with this composition at four different coat weights.

Samples of the paper coated with the composition described above at four different coat weight were each treated with a second coating composition which consisted of a 5% by weight suspension in water of a European bentonite having sodium and calcium exchangeable cations at a coat weight of 0.5 gm^{-2}.

Samples of the coated paper were tested for offset lithography printing properties by means of an IGT Model AC2 printability tester. The paper samples were clipped to the moving sector of the instrument which was set to move at a constant velocity of 1 ms^{-1}. An aluminium alloy damping roll of face width 25 mm and a rubber covered printing roll of face width 20 mm were rotatably and removably mounted on spindles provided on the fixed part of the instrument with the damping roll contacting the surface of the paper sample 70 mm in advance of the line of contact of the printing roll with the paper surface in the sense of the direction of relative motion between the sector bearing the paper sample and the rolls. As a result of this configuration each paper sample was printed with a strip of solid colour 20 mm in width, the first 70 mm being printed on dry paper and the remaining 140 mm on pre-wetted paper. During operation the damping roll was biased against the paper sample with a force of 25 kg and the printing roll was biased against the sample with a force of 50 kg. Both th damping roll and the printing roll had an overall diameter of 68 mm.

Before each test the damping roll was loaded with a substantially identical weight of water, namely approximately 0.6 g of water per square metre of roll surface area by condensation of water vapour on the surface of the roll. The damping roll was placed in a refrigerator having an internal temperature of -8 ± 1°C and a coiled temperature probe connected to a digital thermometer was placed in the central spindle hole of the roll. When the temperature recorded by the thermometer had fallen to +5°C the roll was transferred to a desiccator in which a humidity of 55% RH was maintained by means of a saturated solution of sodium dichromate. When the temperature of the atmosphere in the thermometer had fallen to +5°C the roll was transferred to a desiccator in which a humidity of 55% RH was maintained by means of a saturated solution of sodium dichromate. The temperature of the atmosphere in the laboratory was controlled at 20 ± 1°C. The roll was left in the desiccator for a time of 1 minute 55 seconds and the printability test was performed after another 5 seconds using a printing roll which had been pre-inked with Ault & Wiborg 4-Colour Process Gloss Magenta offset lithography ink.

The block of solid colour printed on the dry and pre-wetted areas, respectively, of the paper samples was tested for print gloss by means of a Hunterlab Glossmeter Model D16 and at an angle of 75° with the normal to the paper surface in accordance with TAPPI Standard No. T480ts-65, the mean of five determinations for each area being recorded.

The block of solid colour printed on the dry and pre-wetted areas, respectively, was also tested for print density by means of a Macbeth RD514 Reflection Densitometer, in this case the mean of ten determinations for each area being recorded.

In addition the gloss of an un-printed area of each coated paper sample was also measured by the TAPPI Standard Method No. T480ts-65.

The results obtained are set forth in Table II below:-

TABLE II

Coat weight of kaolin composition (gm-2)	Coat weight of bentonite composition (gm-2)	Gloss of unprinted paper	Gloss of solid colour area		Print density	
			Dry	Wet	Dry	Wet
2.7	0	7	15	15	1.03	1.04
4.3	0	9	23	21	1.08	1.07
6.2	0	12	30	29	1.14	1.14
8.1	0	13	33	33	1.12	1.13
2.7	0.5	8	20	16	1.04	0.94
4.3	0.5	11	39	23	1.12	0.92
6.2	0.5	14	39	34	1.17	1.00
8.1	0.5	14	38	33	1.15	0.94

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These results show that although the gloss of the un-printed paper for a given coat weight remains substantially the same, there is a significant increase in the gloss of the block of colour printed on the dry area. The print density remains almost unchanged when a top coat of the bentonite composition is applied except for a small decrease in the print density on the pre-wetted area.

EXAMPLE 3

A matt offset printing base paper of substance weight 59 gm^{-2} was coated in two stages, each stage being by means of the laboratory coating apparatus used in Examples 1 and 2 running at a speed of 4000 m min^{-1}.

In the first stage the coating composition used consisted of:

100 parts by weight of natural calcium carbonate
11 parts by weight of a styrene butadiene rubber latex (dry basis)
0.5 parts by weight of sodium carboxymethyl cellulose
0.1 part by weight of sodium hydroxide
water to form a suspension containing 66.9% by weight of total solids.

The natural calcium carbonate was a ground marble having a particle size distribution such that 1% by weight consisted of particles having an equivalent spherical diameter larger than 10 microns and 90% by weight consisting of particles having an equivalent spherical diameter small than 2 microns. The latex contained 50% by weight of styrene butadiene rubber solids.

In the second stage, samples of the paper coated with the above calcium carbonate containing composition were tested with three different suspensions in water of the same bentonite as was used in Examples 1 and 2. The three suspensions contained respectively 4%, 8% and 12% by weight of bentonite, but in each case the coat weight of bentonite actually applied to the paper was about 5 gm^{-2}.

The same offset lithography printing tests as are described in Example 2 were performed on the paper samples coated in two stages and, as a comparison, on a sample coated only with the calcium carbonate containing composition. In addition the gloss of an un-printed area of each coated paper sample was also measured by the TAPPI Standard Method No. T480ts-65.

The results obtained are set forth in Table III below:-

TABLE III

% by weight of bentonite in suspension	Gloss of unprinted paper	Gloss of solid colour area		Print density	
		dry	wet	dry	wet
0	23	44	46	1.28	1.30
4	27	51	51	1.29	1.26
8	28	57	56	1.32	1.29
12	28	57	54	1.36	1.30

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These results show the gloss of the solid colour printed area increases to a greater extent than the gloss of the un-printed paper, both on the dry and on the pre-wetted areas of paper, as the proportion by weight of bentonite in the second coating composition increases. The print density of the solid colour area printed on dry paper also increases although the print density of the solid colour printed on pre-wetted paper remains substantially unchanged.

Claims

1. A paper, suitable for printing, comprising a cellulosic sheet material provided with first and second pigmented coats each of which is hydrophilic, water absorbent and porous, said first coat being a base coat and said second coat being a top coat; wherein the pigment of one of said coats is predominantly of non smectite-type nature, whilst the pigment of the other of the said coats is predominantly of a smectite-type nature comprising at least 60% by weight of a water-swellable smectite-type clay.

2. A paper as claimed in claim 1, wherein the coat comprising predominantly a smectite-type clay as the pigment is the top coat.

3. A paper as claimed in claim 1, wherein the coat comprising predominantly a smectite-type clay as the pigment is the base coat.

4. A paper as claimed in claim 1, 2 or 3, wherein said first and second coats are the only coats provided on the sheet material.

5. A paper as claimed in claim 1, 2 or 3, wherein the sheet material is provided with one or more further coats between said base and top coats.

6. A paper as claimed in any preceding claim, wherein the coat weight of the smectite-type clay coat is no greater than 5 $g.m^{-2}$.

7. A paper as claimed in any preceding claim, wherein one or both of the base and top coats also includes an adhesive.

8. A paper as claimed in any preceding claim, wherein the pigment of said other of the coats comprises at least 75% by weight of the smectite-type clay.

9. A paper as claimed in claim 8, wherein the pigment of said other of the coats comprises at least 90% by weight of the smectite-type clay.

10. A paper as claimed in Claim 2, or any of Claims 3 to 9 when appendant to Claim 2, wherein the pigment of said base coat is predominantly a white pigment other than a smectite-type clay.

11. A paper, suitable for printing, comprising a cellulosic sheet material provided with first and second coats each of which is generally hydrophilic in nature and comprises at least 70% by weight pigment, said first coat being a base coat and said second coat being a top coat, wherein the pigment of the base coat is predominantly of a non-smectite nature and the pigment of the top coat comprises at least 60% by weight of a water-swellable smectite-type clay and forms a coating having a coat weight no greater than 5 $g.m^{-2}$.

12. A paper as claimed in claim 11, wherein the major pigment in the base coat is a white pigment other than a smectite-type clay.

13. A paper as claimed in Claim 12, wherein the major pigment in the base layer is a kaolin clay, a natural or synthetic calcium carbonate, talc or a natural or synthetic calcium sulphate.

14. A method of preparing paper suitable for printing which method includes the steps of applying the following pigmented coats to a cellulosic sheet material;
(i) a first, or base, coat; and
(ii) a second, or top, coat;
wherein the pigment of one of said coats is predominantly of non-smectite-type nature and the pigment of the other of said coats is predominantly of a smectite-type nature comprising at least 60% by weight of a water-swellable smectite-type clay.

15. A method of preparing paper as claimed in claim 14, wherein the pigment of the coat which is predominantly smectite-type in nature is provided by applying to the sheet material an aqueous suspension comprising up to 20% by weight of a pigment comprising at least 60% by weight of a water-swellable smectite clay.

16. A method according to claim 15, wherein the aqueous suspension comprises no greater than 15% by weight of the pigment comprising smectite-type clay.

17. A method of printing an image on a paper, using a rotogravure or an offset lithography printing process, the paper on which the image is printed comprising a cellulosic sheet material provided with first and second pigmented coats each of which is hydrophilic, water absorbent and porous, said first coat being a base coat and said second coat being a top coat; wherein the pigment of one of said coats is predominantly of non smectite-type nature, whilst the pigment of the other of the said coats is predominantly of a smectite-type nature comprising at least 60% by weight of a water-swellable smectite-typ clay.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 3636

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	ABIPC, vol. 57, no. 11, May 1987, page 1607, abstract no. 14651; & JP-A-86 241 183 (EIWA CHEMICAL CO. LTD) 27-10-1986 * Abstract *	1,2,4,7,10-12,14,15	D 21 H 1/22 B 41 M 1/36
A	EP-A-0 192 252 (SÜD-CHEMIE) * Claims 1-3,8,9,12,17,18; examples 3,4 *	1,4,7,14,15,17	
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A	DE-C- 736 450 (J. BAUER et al.)		
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-07-1989	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/FR 98/01872

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H19/82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 440 827 A (MIYAMOTO SHIGEHIKO ET AL) 3 April 1984 see column 2, line 33 - line 54 see column 4, line 62 - column 5, line 9 see examples 1-5 ---	1-6
X	EP 0 634 283 A (CANON KK ;NEW OJI PAPER CO LTD (JP)) 18 January 1995 see page 5, line 43 - line 54 see page 6, line 27 - line 43 see examples III-4 ---	1,2,4-6
X	FR 1 449 148 A (TIME, INCORPORATED) 28 November 1966 cited in the application see the whole document see page 1, column 2, paragraph 6 - page 2, column 1, line 4 ---	1,3-6
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
25 November 1998	02/12/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Songy, O

Form PCT/ISA/210 (second sheet) (July 1992)

Int. .ational Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 337 771 A (ECC INT LTD) 18 October 1989 cited in the application see page 2, line 11 - line 44; example 1	1,4-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

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